HIGH TEMPERATURE METALLOGRAPHIC MICROSCOPE STUDIES OF THE INITIAL OXIDATION OF TANTALUM*

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SUMMARY

High temperature metallographic microscope studies of the initial oxidation of tantalum in the temperature range 300°–1300°C at oxygen pressures of 0.1, 0.01 and 0.001 torr have been carried out. The results are presented as a consecutive series of photographs of specimen surface during the oxidation.

In all cases an incubation period precedes the first visual observation of oxide formation. At any temperature the duration of this incubation period becomes longer the lower the oxygen pressure. During the incubation period oxygen dissolution in the metal is the predominant part-process.

The initial oxide formation, as revealed by the metallographic microscope, never results in a continuous film or scale with an approximately even thickness, but always involves the formation of individual oxide nuclei or crystallites and their subsequent growth. The results are correlated with previous studies of the oxidation of tantalum.

INTRODUCTION

A number of investigators show that tantalum exhibits a complex oxidation behaviour[1-22]. The total oxidation reaction includes oxygen dissolution in the metal and formation of metallic oxide phases (suboxides) and higher oxides. The relative importance of the various part-processes is a function of temperature, oxygen pressure and time of oxidation.

The work described is part of a series of investigations of the oxidation behaviour of tantalum[16-21]. The experimental methods have previously included thermogravimetric measurements of reaction rates, X-ray diffraction studies directly on specimens undergoing oxidation, and examinations of oxidized specimens by means of X-ray and electron diffraction, electron microscopy, metallographic, and microhardness techniques. In the present work high-temperature metallographic microscope studies have been carried out to study directly the initial oxide formation.

MATERIALS AND METHODS

Materials

The tantalum metal was electron-beam melted and supplied by the Wah Chang Corp., U.S.A. in the form of rods with a diameter of 8 mm. The rods were cut into specimens with a length of 10 mm to fit into the high-temperature metallographic microscope. The specimens were recrystallized by a 1/2 h high-vacuum treatment

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($< 10^{-5}$ torr) at 1400°C. Prior to oxidation the specimens were electrolytically polished and etched[23]. The oxygen gas had a purity of 99.8%.

Methods

The high-temperature metallographic studies were made with a Reichert Universal Camera Microscope (Model MeF) with a "Vacutherm" high-temperature attachment[24]. In this unit the specimens are heated indirectly and are placed between two Pt–13% Rh ribbons serving as heating elements. These heating elements permitted observations to be made at specimen temperatures up to 1300°C. The specimen rested on a quartz ring located about 5 mm above a quartz viewing window.

The temperature was measured with a Pt/Pt–10% Rh thermocouple inserted into a hole drilled into the side of the specimen about 1 mm from the surface to be examined.

The specimens were heated in high-vacuum. Due to outgassing of the system pressure rises were observed during the heating-up period, but the pressure was not allowed to exceed 10^{-4} torr. At the higher temperatures the heating period lasted for 20–30 min. During oxidation oxygen was continuously pumped through the system. The pressure was measured with a Leybold Combitron (Penning + Pirani gauge). In no case did the appearance of the specimen surface change during the heating-up period.

RESULTS AND DISCUSSION

Direct examinations of the surface being oxidized were made at temperatures ranging from 300° to 1200°C. At oxygen pressures above 1 torr O_2 and temperatures above 600°C Ta_2O_5-formation was too rapid to give information on the initial oxide formation. Under such conditions the studies were therefore limited to oxygen pressures of 0.1, 0.01, and 0.001 torr.

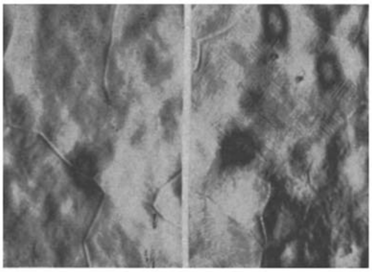
The results are presented as a consecutive series of views of the same surface during the oxidation. In general a large number of photographs were taken for each run. The series of pictures presented below only represent selections with the aim of illustrating the mode of oxide formation and growth of oxide as functions of time under various conditions.

A general feature of all the results is that an incubation period precedes the first visual observation of oxide formation. At any temperature the length of this incubation period becomes longer the lower the oxygen pressure. On the basis of previous studies of the oxidation of tantalum[1,16–21] it is concluded that during this incubation period oxygen dissolution in the metal is the predominant part-process of the total oxidation reaction.

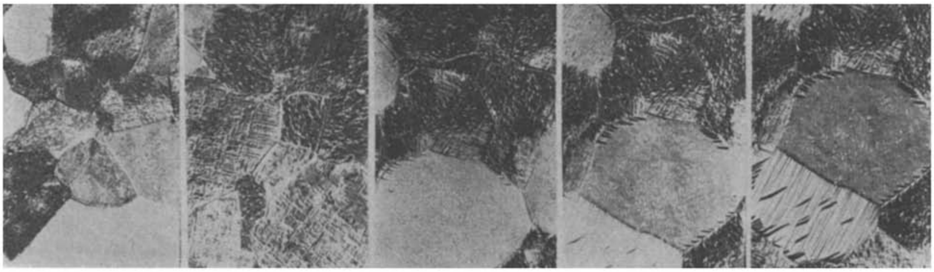
Another general feature is that under none of the conditions employed in the present study did the oxide formation, as viewed under the metallographic microscope, result in a continuous film or scale having an approximately even thickness. The oxide formation always involved the formation of individual oxide nuclei or crystallites and their subsequent growth.

300–500°C

Series 1 shows a tantalum surface oxidized at 300°C and 0.1 torr O_2. The first two micrographs were taken with Nomarski's interference-contrast method. Small changes in the topography become more easily visible with this method than by normal



Start 95 min



209 min 245 min 275 min 420 min 505 min

Series 1. Tantalum oxidized at 300°C and 0.1 torr O_2. The first two micrographs at 86 ×, the rest at 74 ×.

illumination. The second picture of the series shows such small changes in the topography in the form of a regular pattern. In the larger grain the changes appear as lines which intersect at a 90° angle. This pattern is not visible in normal illumination and only occurs when oxygen is introduced into the system.

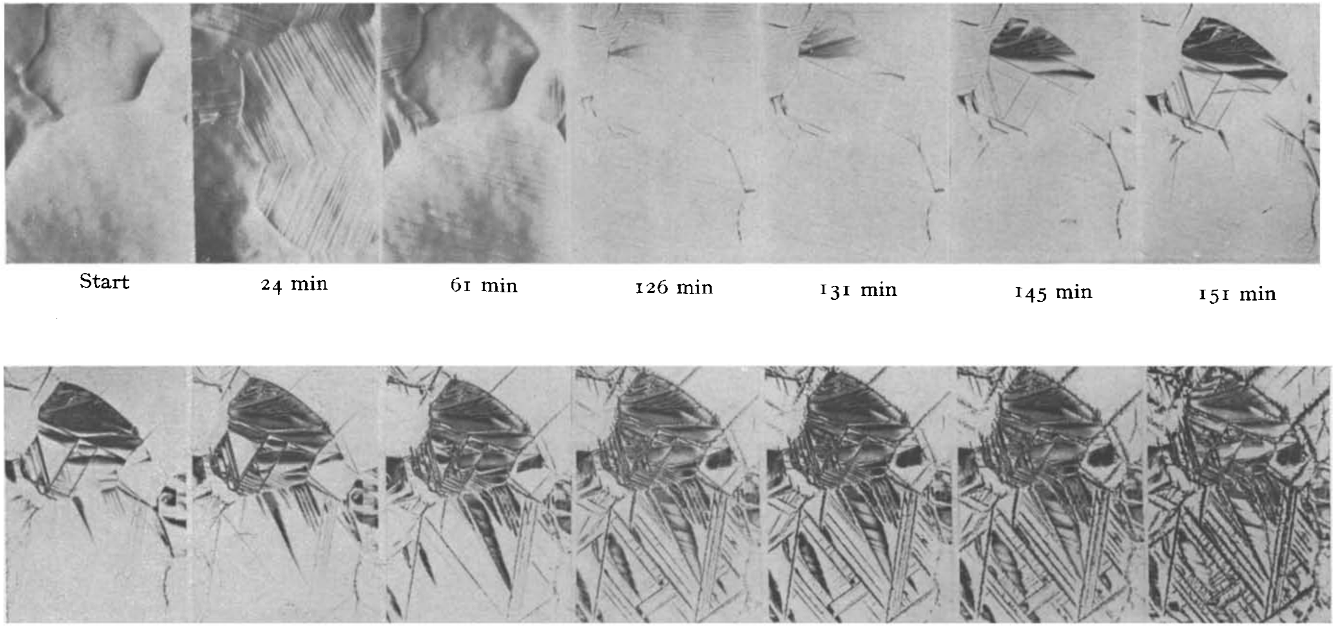
The last five pictures show the surface under normal illumination, the last three showing approximately the same area. The results clearly show the formation of separate oxide phase nuclei or crystallites usually in regular patterns within the individual grains. Furthermore, the rate of nucleation and growth of the oxide phase differs widely from grain to grain.

The results at 400°C and 0.1 torr O_2 (Series 2) qualitatively show a similar type of behaviour. The first three pictures, taken by the interference-contrast method, show the changes in topography in the form of lines traversing the grains. After more extended oxidation (126 min) the first formation of oxide readily detectable under normal illumination becomes evident. Compared with the results at 300°C fewer oxide nuclei are formed and the oxide phase formation to a large extent occurs through growth which spreads out from a few points or areas on the surface.

Previous studies of oxidation of tantalum have shown that the reaction at 300°–400°C may be represented by

$$1/2\,\overset{(g)}{O_2} \longrightarrow O_{\text{chemisorbed}} \xrightarrow{\text{diffusion}} \text{Ta–O sol.sol'n} \rightarrow TaO_y \rightarrow TaO_z$$

The oxidation thus involves an oxygen dissolution in the metal followed by the formation of the metallic oxide phases, TaO_y and TaO_z. No Ta_2O_5 has been detected on the surface under these conditions for oxidation periods of up to 4600 min[19].



Series 2. Tantalum oxidized at 400°C and 0.1 torr O_2. The first three micrographs at 86 ×, the rest at 74 ×.

TaO_y has previously only been detected by X-ray diffraction, and metallographically it has not been possible to differentiate this phase from the metal[17,18]. PAWEL, CATHCART AND CAMPBELL[14] have shown that TaO_z grows as platelets parallel to {320} sets of planes of the metal lattice. This has also been substantiated in previous studies in the present series of investigations[18].

It is proposed that the line patterns observed with the interference-contrast method in the present work may possibly reflect the formation of TaO_y. As an alternative interpretation CATHCART[25] has suggeested that the line patterns reflect deformation of the metal due to dissolution of oxygen. From the previous studies[16-19] it is concluded that the second phase, observed under normal illumination, is identical with TaO_z.

All in all the studies clearly demonstrate the great importance of oxide nucleation and growth of oxide crystallites in the oxidation of this metal. It is not unreasonable to assume that these processes in fact determine the rate of oxidation when there is an excess supply of chemisorbed oxygen atoms on the surface. One of the authors[19] has proposed that such processes may give rise to the approximately logarithmic oxidation observed during the initial stages of oxidation of tantalum at 300°–400°C at 1 atm O_2. The observed behaviour also explains the difficulty in obtaining good reproducibility in weight gain studies of oxidation rates under these conditions. Furthermore, it is not unlikely that sudden changes in oxidation rates might be observed if the measurements were made with sensitive balances.

At 300°–400°C there are small differences in the appearance of the specimens when oxidizing at 0.1 torr and 1 atm O_2. However, at 1 atm a very marked rise in the temperature of the specimen occurred immediately after introducing the oxygen in the chamber. Thus at 450°C and 1 atm O_2 the temperature of the specimens increased from 50° to 80°C during the first minute after filling the apparatus with oxygen gas. The temperature decreased to the present value after 3–4 min of oxidation. No corresponding temperature change was observed at 0.1 torr O_2. It is believed that this temperature change is due to heat of chemisorption and heat of solution of oxygen in the metal. Such temperature changes will of course greatly influence the rate of oxidation during the very initial stage and care must be taken in interpreting the reaction kinetics during such periods. Such effects will also become more serious the higher the surface/volume ratio.

Although Ta_2O_5 has not been observed at 300°–400°C, this oxide will form if the oxidation is carried out for sufficiently long periods of time. This incubation period becomes shorter the higher the temperature. Thus, at 500°C and 1 atm O_2 the duration of this incubation period as determined from weight gain studies amounts to 150 to 250 min, while at 600°C is too short to be observed thermogravimetrically and probably is of the order of a few minutes[16]. Also the incubation period generally becomes longer the lower the oxygen pressure.

500–800°C

At 500°–800°C the incubation period for the Ta_2O_5 formation involves the reaction scheme in eqn. (1)[16,21]. It is possible that TaO_z is formed directly from Ta–O solid solutions under these conditions as TaO_y have not been detected on specimens oxidized above 500°C[18].

The various features of the initial oxidation of tantalum at 500°–800°C at oxygen pressures of 0.1, 0.01, and 0.001 torr are shown in series 3–8. At 500°C and 0.1 torr O_2 (Series 3) no oxide formation is observed during the initial stage. The first trace of TaO_z is observed after 13 min and after 60–70 min the TaO_z formation becomes rapid. After more extended oxidation Ta_2O_5 forms on the TaO_z platelets (272 min). This mode of Ta_2O_5 formation results in a porous oxide scale with little or no protective properties[17].

It is difficult to photograph the oxide formation when thick oxide scales are formed. Under these conditions the oxide surface becomes more uneven and one has difficulties in focusing on the whole surface. Such studies also show that the surface of the thicker Ta_2O_5 scales continuously cracks, breaks up, and exhibits slight movements during the oxidation. This is in all probability due to the much higher molar volume of the oxide (ratio of oxide volume/metal volume is 2.5) which further adds to the porosity and non-protectiveness of the scale.

An equivalent behaviour is observed at 600°C and 0.01 torr O_2 (Series 4). The effect of oxygen pressure at 600°C is clearly evident by comparing Series 4 and 5, the latter results referring to a run at 0.001 torr O_2. At the lower pressure no TaO_z formation is observed after 100 min compared to approximately 20 min at 0.01 torr O_2. It should also be noted that at the lower oxygen pressure the initial TaO_z formation preferentially occurs at grain boundaries and grows out from points or defects in the metal.

At 800°C and 0.1 torr O_2 (Series 6) it is seen that the surface is fully covered with Ta_2O_5 after 4 min. This is to be compared with the results at 500°C and the same oxygen pressure where 270 min were needed to achieve approximately the same oxide coverage. By lowering the oxygen pressure at 800°C, the incubation period for the oxide formation is again increased (Series 7).

Corresponding studies at 700°C gave results similar to those at 600° and 800°C.

800–1200°C

At about 800°C a change in the oxidation mechanism takes place[21]. Above this temperature TaO rather than TaO_z gradually becomes the intermediate reaction product. The reaction thus changes to

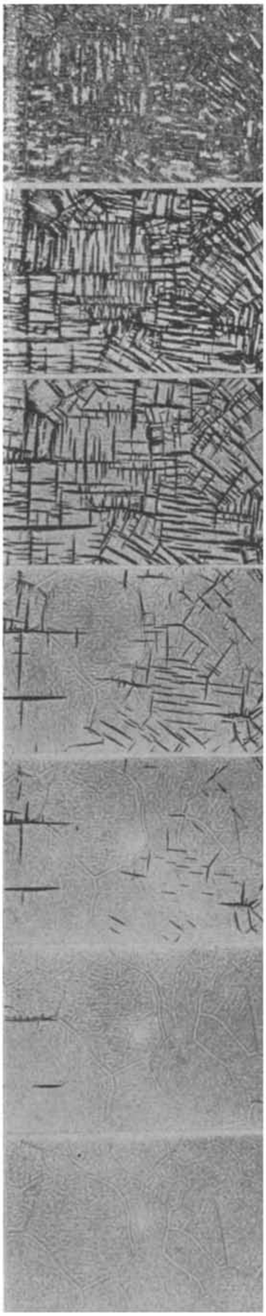
$$\text{Ta-O sol.sol'n} \rightarrow \text{TaO} \rightarrow \text{Ta}_2\text{O}_5$$

This change is also reflected in a change in the mode of oxide formation above 800°C. This is shown in Series 8–18.

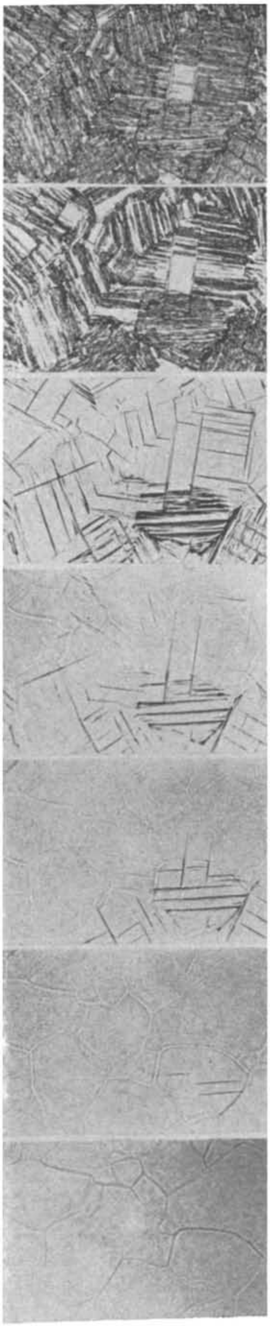
Series 8 shows a specimen (heavily etched) oxidized at 900°C and 0.1 torr O_2. The characteristic pattern of TaO_z platelet formation is no longer observed; rather the oxide formation occurs more evenly over the grains in the metal. At 0.01 torr O_2 at the same temperature (Series 9) the same feature is also evident. These results also suggest TaO_z-formation as evidenced by the darker lines traversing the grains. An alternative interpretation may be that these lines represent twinning in the metal.

At 0.001 torr (Series 10) TaO_z appears to be formed. The relative importance of the TaO *versus* TaO_z formation thus seems to be dependent upon oxygen pressure and TaO_z platelet formation appears to be favoured at low oxygen pressures. The results at 0.001 torr O_2 also suggest that the relative rates of formation of the two oxide phases may also depend on the orientation of the individual grains.

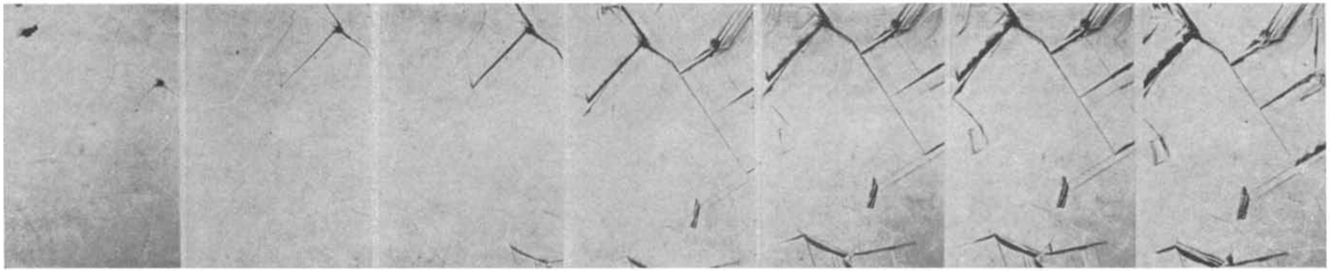
The general behaviour at 1000°C resembles that at 900°C as shown in Series 11–14. At 0.1 torr O_2 a more even oxide formation over the grains occurs, while at 0.01 torr O_2 (Series 12) the results suggest twinning or possibly TaO_z-formation. Series 13 and 14 show the results of two different runs at 0.001 torr O_2. In both runs the initial



Series 3. Tantalum oxidized at 500°C and 0.1 torr O_2. 74 ×.

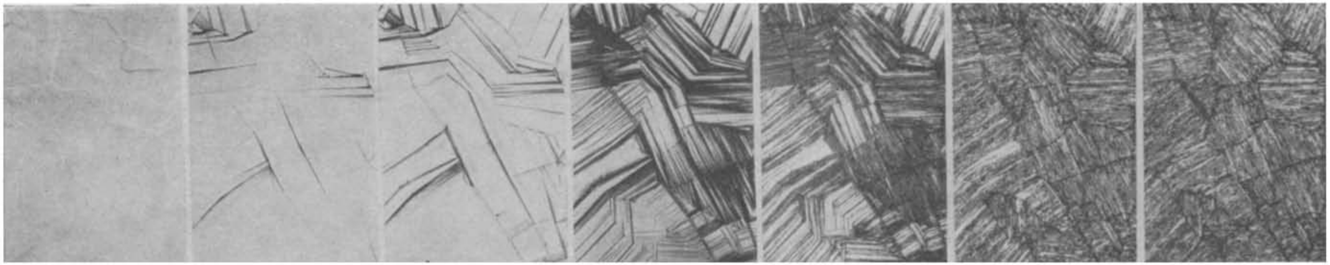


Series 4. Tantalum oxidized at 600°C and 0.01 torr O_2. 74 ×.



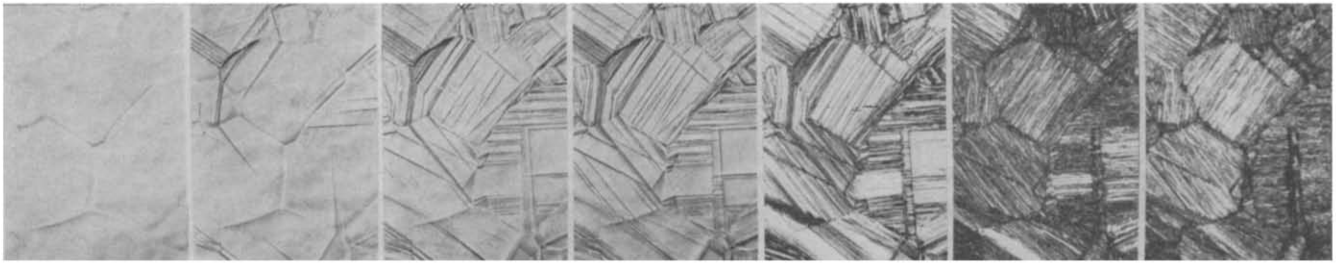
103 min 152 min 213 min 273 min 303 min 348 min 393 min

Series 5. Tantalum oxidized at 600°C and 0.001 torr O_2. 74 ×.



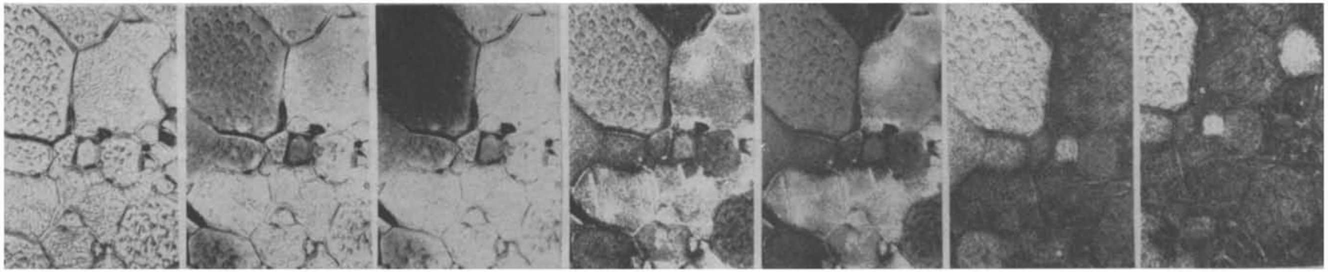
Start 20 sec 40 sec 70 sec 115 sec 3 min 4 min

Series 6. Tantalum oxidized at 800°C and 0.1 torr O_2. 74 ×.



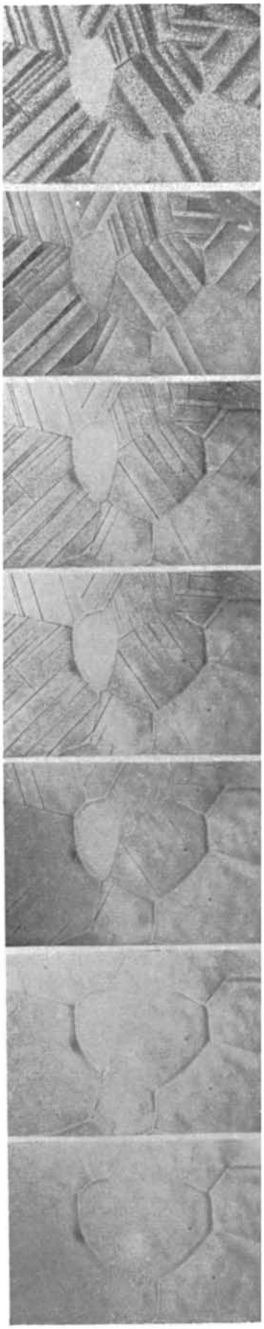
Start 1.5 min 2 min 2.5 min 4.5 min 8.5 min 52 min

Series 7. Tantalum oxidized at 800°C and 0.01 torr O_2. 74 ×.

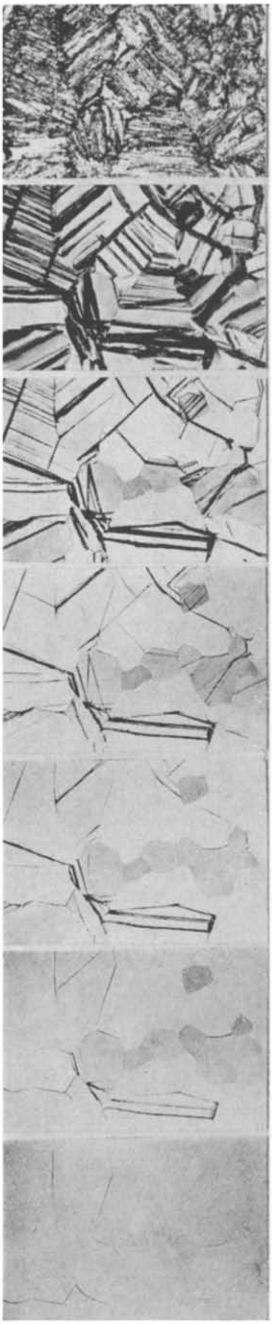


Start 1 min 2 min 3 min 3.5 min 10 min 21 min

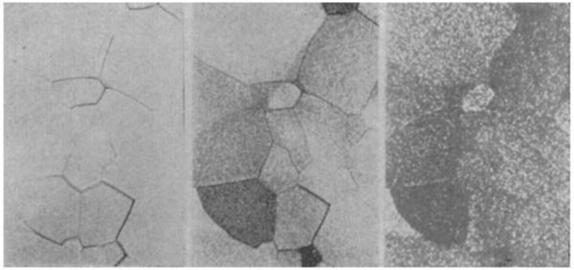
Series 8. Tantalum oxidized at 900°C and 0.1 torr O_2. 74 ×.



Series 9. Tantalum oxidized at 900°C and 0.01 torr O_2. 74 ×.

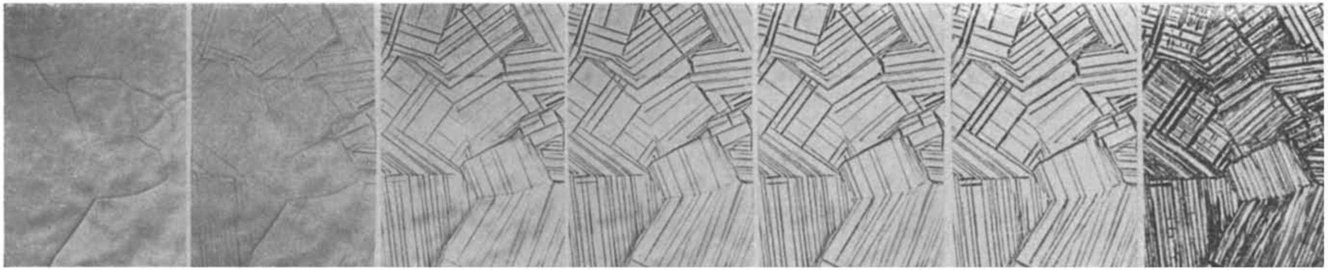


Series 10. Tantalum oxidized at 900°C and 0.001 torr O_2. 74 ×.



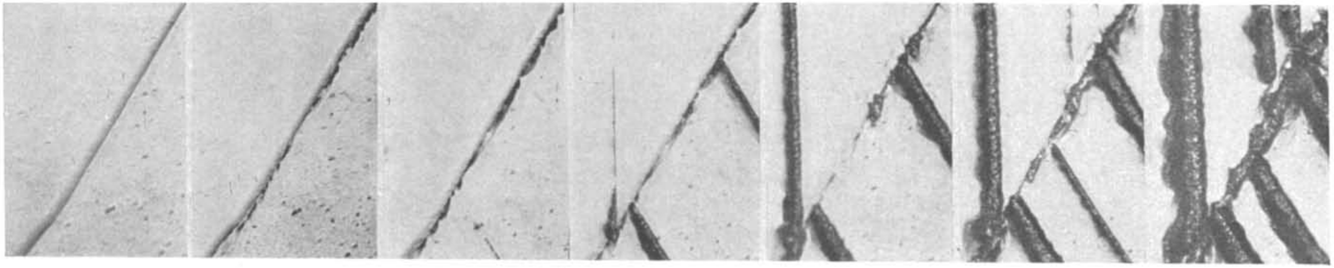
Start 2 min 4 min

Series 11. Tantalum oxidized at 1000°C and 0.1 torr O_2. 74 ×.



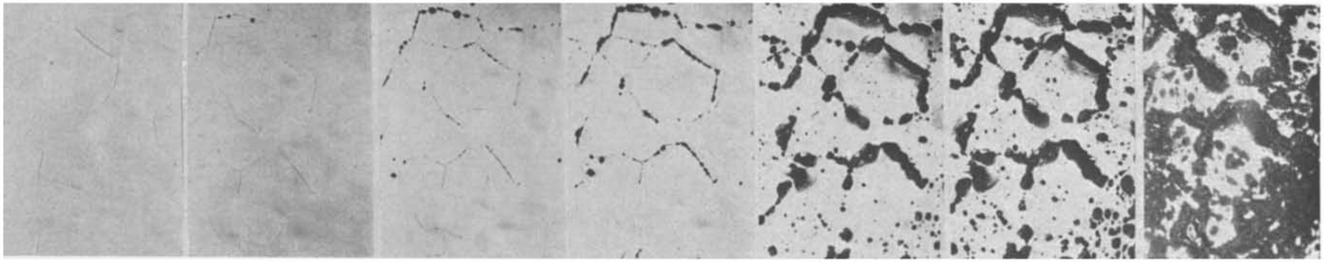
Start 100 sec 105 sec 110 sec 115 sec 120 sec 130 sec

Series 12. Tantalum oxidized at 1000°C and 0.01 torr O_2. 74 ×.



Start 105 min 163 min 168 min 175 min 182 min 195 min

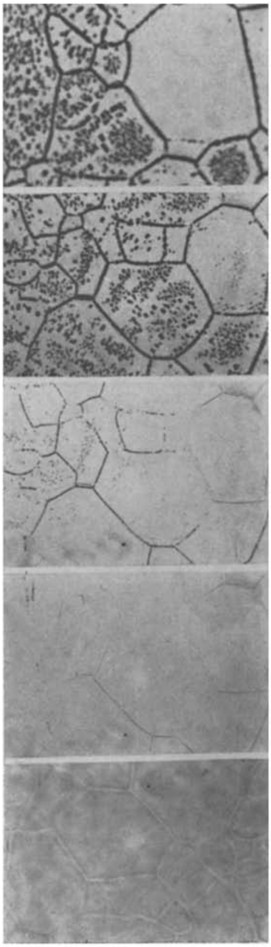
Series 13. Tantalum oxidized at 1000°C and 0.001 torr O_2. 134 ×.



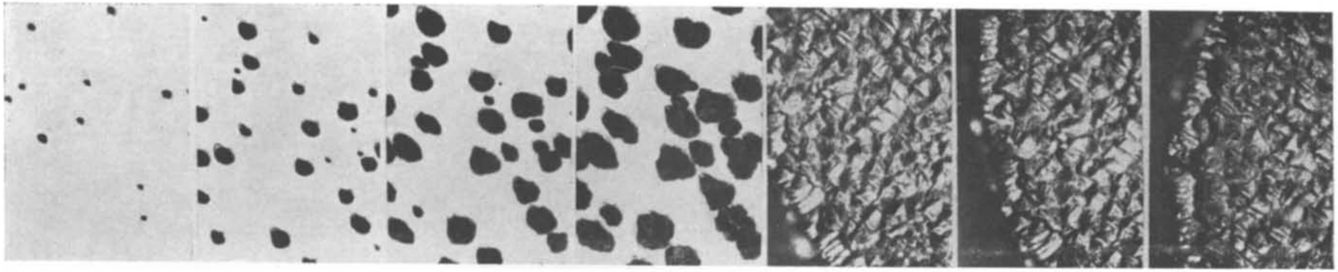
Start 238 min 243 min 248 min 258 min 273 min 308 min

Series 14. Tantalum oxidized at 1000°C and 0.001 torr O_2. 74 ×.

Series 15. Tantalum oxidized at 1100°C and 0.001 torr O_2. 134 ×.
The 55 sec micrograph is taken with darkfield illumination.

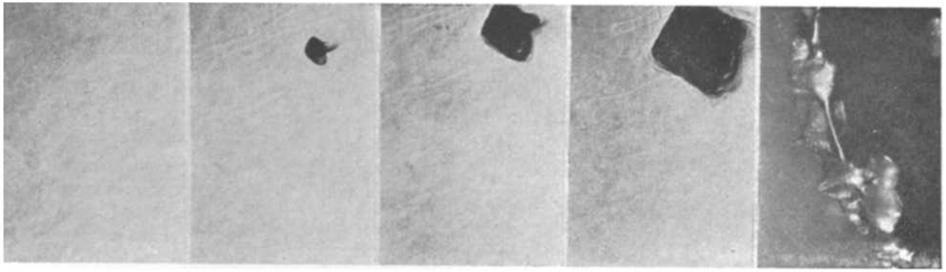


Series 16. Tantalum oxidized at 1150°C and 0.01 torr O_2. 74 ×.



4 min 7 min 9 min 10 min 40 min 46 min 60 min

Series 17. Tantalum oxidized at 1200°C and 0.01 torr O_2. The first four micrographs at 74 ×, the rest at 36 ×.



10 min 27.5 min 30 min 41 min 75 min

Seires 18. Tantalum oxidized at 1200°C and 0.001 torr O_2. The 75 min micrograph taken with darkfield illumination.

oxide formation is favoured at grain boundaries, but otherwise the modes of oxide formation are appreciably different. Again the orientation of the grains may affect the relative rates of formation of different oxide phases. The results at 0.001 torr O_2 also illustrate the difficulties in reproducing the exact mode of oxide formation; only the general features are the same.

At 1100°–1200°C there is no evidence of twinning or platelet formation (Series 15–18). The oxide formation occurs as individual nuclei or cystallites. The number and size of the oxide crystallites is a function of temperature and oxygen pressure. Thus, by comparing Series 17 and 18 — referring to runs at 1200°C it is seen that the number of nuclei becomes smaller but the size of each crystallite is larger the lower the oxygen pressure. The same tendency is observed with increasing temperature as is seen by comparing Series 15 and 18 which refer to series made at 0.001 torr O_2 at 1100° and 1200°C, respectively. A detailed examination of the pictures also reveals deformation in the metal around each nucleus. In one run platelet formation was observed during cooling of the specimen.

The results at 1100°–1200°C clearly emphasize the importance of nucleation and growth processes in governing the rate of oxidation and in understanding the oxidation mechanism during the initial stages. The occurrence of a smaller number but larger size of crystallites with increasing temperature is in agreement with the general theory of nucleation and growth of nuclei in that the rate of nucleation decreases but the rate of growth of each nucleus increases with temperature.

The present work has been of a qualitative and descriptive nature. Despite this it is felt that such studies provide important information and offer distinct possibilities in understanding the oxidation behaviour of metals. To put such studies on a more quantitative basis an obvious path to follow would be to use single crystals and to study the oxide formation as a function of crystal orientation. Excellent work on the TaO_z-platelet formation during oxidation at 500°C using this approach has been published by PAWEL *et al.*[14].

ACKNOWLEDGEMENTS

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